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PREPARATION OF YTTRIUM FLUORIDE

USING AMMONIUM BIFLUORIDE

by

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PREPARATION OF YTTRIUM FLUORIDE USING AMMONIUM BIFLUORIDE

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I INTRODUCTION

The possibility of preparing pure yttrium fluoride by reacting yttrium oxide with ammonium bifluoride, $\text{NH}_4\text{F} \cdot \text{HF}$ (ammonium acid fluoride), has been investigated. Earlier work was done at the Ames Laboratory by A. H. Daane.¹ The main reaction between ammonium bifluoride and yttrium oxide is believed to be as follows:

The main advantages of this method and, therefore, the principal reasons for studying the reaction are: (1) this method of preparing pure yttrium fluoride would eliminate the difficult handling problems involved with the use of anhydrous hydrofluoric acid and (2) the process could be scaled up for large scale production quite easily.

¹ F. H. Spedding and A. H. Daane, "The Preparation and Properties of the Rare Earths", Progress in Nuclear Energy, Series V, Chapter 5, H. M. Finneston and J. P. Howe, eds., McGraw-Hill Book Co., Inc., N. Y. (1956).

II EXPERIMENTAL RESULTS - Small Scale Runs

The equipment used for these runs consisted of a 3 1/2 inch I. D. graphite crucible heated by a vertical tube-type resistance furnace, a chromel-alumel thermocouple placed in a graphite well in the center of the crucible, inlet and outlet tubes at the top of the crucible for passing an inert gas through the system to sweep out the reaction products, and a means of condensing the reaction products.

Except for the hydrofluoric acid topping runs where a twenty gram charge was used, flaked ammonium bifluoride was ground with a mortar and pestle and mixed, in varying amounts, with 100 grams of yttrium oxide or yttrium fluoride. In all runs, the charge was raised to an initial low temperature and held for two hours to obtain the desired reaction and remove ammonia and water, and then raised to 400°C for the remainder of an eight hour period to drive off the remaining ammonium fluorides. A stream of air or inert gas was passed into the crucible to sweep out the vapors.

The product fluoride was sampled as near the center of the charge as possible and the remaining fluoride subsequently removed from the crucible. Both samples of the soft, white, generally porous, chalk-like yttrium fluoride were powdered between two sheets of polyethylene

film, placed in glass sample bottles and submitted for oxygen intensity ratio analysis. The center sample comprised approximately 10 per cent by weight of the total product fluoride. The remainder of the product was labeled "mixture" sample. The oxygen intensity ratios for the "mixture" samples are reported in all cases except for the section giving the results of the effects of varying conversion temperature and mole ratio of ammonium bifluoride to yttrium oxide on the oxygen intensity ratio of the product yttrium fluoride. In this section a weighted average of the two analyses was reported. Oxygen intensity ratios for the "center" samples were generally about the same as those for the "mixture" samples.

Reaction Temperature and Mole Ratio of Ammonium Bifluoride to Yttrium Oxide

The main reaction between yttrium oxide and ammonium bifluoride was assumed to be as given on Page 1. However, it appears that the water and ammonium fluoride reaction products interact to form ammonium hydroxide and ammonium bifluoride since it was noted that the vapors being flushed from the system were quite basic and the odor of ammonia was quite strong. The mole ratio of ammonium bifluoride to yttrium oxide was varied from 6:1 to a 100 per cent

excess or a 12:1 ratio. The initial reaction temperature was varied between 100°C and 280°C. This temperature range was from approximately 30°C below the melting point to approximately 40°C above the boiling point of ammonium bifluoride. The oxygen intensity ratios from all runs in this series are shown on the graph in Figure 1.

It appears that the 9:1 mole ratio runs resulted in a generally lower oxygen intensity ratio fluoride, with 130°C to 140°C being the approximate optimum conversion temperature. It was theorized that since this temperature was slightly above the melting point of the ammonium bifluoride, intimate contacting of the yttrium oxide by the ammonium bifluoride was effected with a minimum loss of ammonium bifluoride. This, however, does not explain the low oxygen intensity ratio fluorides prepared at other temperatures; especially those at approximately 230°C for the 6:1, 7:1 and 9:1 mole ratios.

Vacuum Conversion

Attempts were made to improve the conversion by applying a vacuum to facilitate the removal of water and ammonia reaction products from the system at a low temperature. A stainless steel vacuum crucible was fabricated and lined with a graphite crucible

Fig. 1 Oxygen Intensity Ratio of Yttrium Fluoride vs. Initial Conversion Temperature for Various Mole Ratios of Ammonium Fluoride to Yttrium Oxide.

to contain the charge. A vacuum of approximately 28 inches of mercury was applied during the two hour, low temperature conversion period and then the ammonium fluoride and excess ammonium bifluoride were driven off at 400°C by sparging with argon at atmospheric pressure. During the vacuum period, a concentrated ammonium hydroxide solution was driven off and condensed in an acetone-dry ice cold trap. The oxygen intensity ratios for these runs are reported in Table I. Conversion

Table I

Oxygen Intensity Ratios for Yttrium Fluorides Produced by Reacting
Yttrium Oxide with Ammonium Bifluoride Under a Vacuum

Reaction Temperature, °C	Moles $\text{NH}_4\text{F} \cdot \text{HF}$ Mole Y_2O_3	Oxygen Intensity Ratio
100-110	6	0.56
100-120	6	0.58
100-115	7	0.42
100-115	7	0.36
100-130	7	0.64
130-140	7	0.29
100-105	9	0.47
100-115	9	0.58

seems to be most efficient at 100 to 115°C using seven moles of ammonium bifluoride per mole of yttrium oxide. These results indicate a significant improvement in the oxygen intensity ratios of the fluorides produced with the use of a vacuum. It was noted, however, that considerable ammonium bifluoride or ammonium fluoride was volatilized from the charge during the two hour vacuum period for the 130-140°C conversion run. Therefore, 140°C is probably the maximum usable temperature for vacuum conversion runs.

Effects of Using Different Gases for Sweeping Out Reaction Products

To assist in the removal of gaseous reaction products, an inert gas was injected into the crucible to sweep out these vapors. The effectiveness of only two gases was evaluated, high purity argon and air. The purity of the argon used was 99.99 per cent, which essentially eliminated the possibility of adding impurities to the product through this gas stream. Samples of yttrium oxide and ammonium bifluoride were reacted at 130 to 140°C using nine moles of bifluoride per mole of oxide. The average oxygen intensity ratios reported for two runs at these conditions were 0.37 and 0.41. These values were compared with those from two identical runs using dry air as a sparging medium.

The intensity ratios reported for these runs were 0.37 and 0.66.

Since these two values were inconsistent, both samples were submitted for reanalysis. These results varied greatly from the original ones making it quite difficult to draw reliable conclusions. It appears, however, that the use of an inert, oxygen-free gas for sparging is necessary if oxygen contamination of the fluoride is to be kept at a minimum. A summary of the results of these runs is presented in Table II.

Table II

Oxygen Intensity Ratios for Yttrium Fluorides Produced
by Reacting Yttrium Oxide with Ammonium Bifluoride
and Using Air and Argon as Sparging Mediums
to Sweep Reaction Products from the Crucible

Sparging Medium	Reaction Temperature °C	Oxygen Intensity Ratios			
		1st anal.	2nd anal.	3rd anal.	Average
Argon	130-140	0.37			
Argon	130-140	0.42			
Air	130-135	0.37	0.58	0.55	0.50
Air	130-145	0.66	0.41	0.54	0.54

Nitrogen, with a purity of over 99.5 per cent can be obtained commercially for approximately one-sixth the cost of argon. The impurities contained in the nitrogen include only a very small amount of oxygen. Since the purity of the nitrogen is nearly equal to that of the argon used, the use of this gas as a sparging medium might be a satisfactory alternate for argon.

Effects of Finely Grinding the Ammonium Bifluoride

To obtain more intimate contact between the yttrium oxide and ammonium bifluoride and possibly better conversion, the bifluoride was ground with a hammer-mill to approximately 200 mesh. Several runs were made at 130 to 135°C using various quantities of this material. The oxygen intensity ratios for these runs are reported in Table III. The first two runs made (the first and third in the table)

Table III

Oxygen Intensity Ratios for Yttrium Fluoride Produced by
Reacting Yttrium Oxide with Finely Ground Ammonium Bifluoride

Reaction Temperature °C	Moles $\text{NH}_4\text{F} \cdot \text{HF}$ Mole Y_2O_3	Oxygen Intensity Ratios			
		1st anal.	2nd anal.	3rd anal.	Average
130-135	7	0.23	0.54	0.56	0.44
130-145	7	0.57	0.41	0.54	0.51
130-135	9	0.39	0.46	0.62	0.49
130-145	9	0.60	0.51	0.50	0.54

indicated a slight improvement in the oxygen intensity ratio with grinding, however, when the runs were duplicated, the results were very high. The samples were, therefore, reanalyzed. Although it was difficult to obtain good rechecks on the analyses, there appears to be no advantage in grinding the bifluoride.

Effects of Fluoride Particle Size

The importance of using small fluoride particles in topping runs was also investigated. A sample of high oxygen intensity ratio yttrium fluoride prepared by hydrofluorination of yttrium oxide using anhydrous hydrofluoric acid was topped with ammonium bifluoride at 130 to 140°C using nine moles of bifluoride per mole of yttrium fluoride. Then, a sample of the same fluoride was ground with a hammer-mill and topped with ammonium bifluoride in a similar manner. The oxygen intensity ratios for these fluorides are shown in Table IV. Topping the fine fluoride particles gave lower oxygen intensity ratios than topping the coarse particles, indicating the importance of grinding the fluoride before topping.

Effects of Oxide Particle Size

The importance of finely grinding the yttrium oxide before contacting it with ammonium bifluoride was investigated by screening samples of

Table IV
Oxygen Intensity Ratios for Yttrium Fluoride Produced by
Topping Ground and Unground Yttrium Fluoride with
Ammonium Bifluoride Using Nine Moles of Bifluoride
per Mole of Yttrium Fluoride

Reaction Temperature, °C	Particle Size	Oxygen Intensity Ratios
130-135	unground, large particles, OIR of YF_3 before topping = 0.64	0.46
130-145	unground, large particles, OIR of YF_3 before topping = 0.64	0.63
130-135	ground by hammer-mill, small particles, OIR of YF_3 = 0.64	0.36
130-140	ground by hammer-mill, small particles, OIR of YF_3 = 0.64	0.41

oxide and reacting the +200 and the -270 mesh particles. These particles were reacted at 130 to 140°C using nine moles of bifluoride per mole of oxide. The results of these runs are shown in Table V. Generally, the results do not indicate that the fine particles are more easily and completely

Table V

Oxygen Intensity Ratios for Yttrium Fluorides Produced by
Reacting Different Size Yttrium Oxide Particles with
Ammonium Bifluoride Using Nine Moles of Bifluoride
per Mole of Oxide

Reaction Temperature, °C	Particle Size	Oxygen Intensity Ratios			
		1st anal.	2nd anal.	3rd anal.	Average
130-140	-270 mesh	0.38	0.54	0.62	0.51
135-145	-270 mesh	0.59	0.42	0.51	0.54
130-145	+200 mesh	0.45	0.53	0.63	0.54
130-140	+200 mesh	0.36	0.31	0.41	0.36

converted to yttrium fluoride than coarse particles. This is inconsistent with results from hydrofluorination runs using anhydrous hydrofluoric acid, and is contrary to the belief that the oxide particles become coated with a fluoride film making complete conversion of large particles of oxide to the fluoride difficult.

Topping of Yttrium Fluoride

Attempts were made to lower the oxygen intensity ratios of yttrium fluorides produced by the reaction of Y_2O_3 with $NH_4F \cdot HF$ by recontacting

the fluoride with a fresh quantity of ammonium bifluoride. The oxide conversion run and subsequent topping run were both made at 130-140°C using a 7:1 mole ratio of ammonium bifluoride to yttrium oxide and yttrium fluoride, respectively. No improvement in the oxygen intensity ratios was noted after topping.

Topping with Anhydrous Hydrofluoric Acid

Attempts were made to lower the oxygen intensity ratios of fluorides prepared by the foregoing methods by topping with anhydrous hydrofluoric acid for eight hours at 600°C. Twenty gram samples were hydrofluorinated in a platinum boat. Fluoride was topped directly with anhydrous hydrofluoric acid and also blended with ammonium bifluoride and topped with anhydrous hydrofluoric acid. The same runs were carried out using yttrium oxide in place of yttrium fluoride. Oxygen intensity ratios reported for all samples were approximately 0.43. Therefore, it was concluded that there is no advantage in topping yttrium fluoride from the ammonium bifluoride runs with anhydrous hydrofluoric acid to lower the oxygen content.

III EXPERIMENTAL RESULTS - Large Scale Runs

The size of the graphite crucible used in the small scale run was only large enough to react 300 grams of oxide with ammonium bifluoride

at a nine to one mole ratio. One run was made using 300 grams of oxide. The average oxygen intensity ratio for samples taken from this run was about 0.40, which is essentially the same as those values obtained in smaller size runs.

To further evaluate the effect of the size of charge, the crucible size was increased from 3 1/2" I.D. by 12" deep to 5 3/4" I.D. by 18" deep. Four runs were made with this equipment using four pounds of yttrium oxide in each run. Conditions found to be most favorable in the small-scale runs were used in these runs. The charge for runs I and III was a mixture of seven moles of ammonium bifluoride per mole of yttrium oxide while the mole ratio in runs II and IV was nine to one. The charges were held at the conversion temperature for two hours and the temperature then raised to 400°C and sparged with argon until all of the ammonium fluoride and excess ammonium bifluoride was driven off. At this temperature, at least 12 hours were necessary for complete removal of the ammonium fluoride and bifluoride. The charges were then cooled under a flow of argon and samples taken from the center and edge of the crucible at the top, middle and bottom of the charge. The oxygen intensity ratios for these samples are presented in Table VI. The high oxygen intensity ratios reported and

Table VI

Oxygen Intensity Ratios for Yttrium Fluoride Produced by
Reacting Four Pounds of Yttrium Oxide with Ammonium
Bifluoride at Various Temperatures and Mole Ratios

Run Number	I	II	III	IV
Mole Ratio	7:1	9:1	7:1	9:1
Conversion Temp., °C	230	135	230	135
Oxygen Intensity Ratios				
Top edge	0.55	0.27	0.30	0.26
Top center	0.64	0.31	0.40	0.26
Middle edge	0.32	0.34	0.35	0.28
Middle center	0.50	0.34	0.31	0.34
Bottom edge	0.31	0.38	0.25	0.34
Bottom center	0.34	0.34	*0.79	0.38
Average	0.44	0.33	0.32	0.31

* This value was not included in the average

also the crusty nature of several of the samples in Run I indicated that removal of the ammonium fluoride and bifluoride was not complete in

certain portions of the charge. The presence of ammonium compounds interferes with the oxygen intensity ratio analytical method. Lower oxygen intensity ratios were obtained from samples taken at points in the charge near the walls of the crucible where the temperature was highest and removal of ammonium fluoride and bifluoride probably more complete. These samples were more chalk-like. The single high oxygen intensity ratio reported in Run III was assumed to be in error and was therefore not considered in evaluating the results. The average oxygen intensity ratios for Runs II, III and IV indicate that there is very little difference in the yttrium fluorides produced at 135°C using a nine to one mole ratio and that produced at 230°C using a seven to one mole ratio. However, the time required and the difficulty involved in completely removing the reaction products might make the 7:1 mole ratio more desirable.

The yttrium fluoride from each of the four runs was reduced to yttrium metal by Metallurgy Group V at this Laboratory and the metal analyzed to more accurately establish the quality of the fluoride. Each reduction sample was 1500 grams. The metal samples were then analyzed by the spectrographic group. The reported analyses for oxygen, carbon, nitrogen and fluorine are shown in Table VII.

Table VII

Analysis of Yttrium Metal Produced by Reduction of Yttrium
Fluoride from Large-Scale Yttrium Oxide-Ammonium
Bifluoride Runs

Run Number	Oxygen Intensity Ratio of YF_3	Analysis in ppm			
		Oxygen	Carbon	Nitrogen	Fluorine
I*	0.44	2740	721	240	1956
II	0.33	2620	185	179	1727
III	0.40	2470	239	176	1585
IV	0.31	2420	127	216	1328

* This was the first run made with the graphite crucible, so the carbon analysis for the product fluoride was quite high.

The oxygen values were slightly higher than those values usually obtained by reducing yttrium fluoride from anhydrous hydrofluoric acid-yttrium oxide hydrofluorination runs and having approximately these oxygen intensity ratios. The expected value is around 2000 to 2200 ppm for yttrium fluoride having an oxygen intensity ratio of 0.30 to 0.35. The difference could be attributed to unreliable oxygen intensity ratio values

which might have been the result of interferences caused by the presence of impurities in the sample. Generally, carbon and nitrogen analyses were about the same as those for metal produced by reducing the fluoride from yttrium oxide-anhydrous hydrofluoric acid runs.

IV DISCUSSION

A very low oxygen intensity ratio yttrium fluoride (0.25 to 0.35 or lower) could not be consistently produced by any of the methods investigated. Very inconsistent oxygen analyses of the fluoride samples made it difficult for reliable conclusions to be drawn. Conditions most favorable for the reaction between yttrium oxide and ammonium bifluoride, which results in a fluoride with an oxygen intensity ratio of approximately 0.40 were as follows:

- (1) nine moles of bifluoride per mole of oxide reacted at 130°C
- (2) seven moles of bifluoride per mole of oxide reacted at 230°C
- (3) seven moles of bifluoride per mole of oxide reacted at 100 to 115°C, using a vacuum to pull off water, ammonia and other reaction products formed during the initial reaction period.

The conditions indicated in (2) would probably be most practical since the temperature must be raised to 400°C after the reaction has taken place

to drive off the excess ammonium bifluoride and ammonium fluoride, and smaller amounts of ammonium bifluoride would be required.

However, it is possible that condition (3) would result in a slightly lower oxygen content yttrium fluoride, since more of the oxygen bearing reaction products would be removed at low temperatures, thus offering less chance for the formation of yttrium oxyfluoride.

The use of an inert gas such as argon for sweeping reaction products from the crucible and grinding the yttrium fluoride before topping, were other conditions found to be favorable in the preparation of low oxygen intensity ratio yttrium fluorides.

As the diameter of the crucible is increased, uniform heating of the charge becomes increasingly difficult. This makes efficient and complete removal of the reaction products quite difficult. Therefore, if this method were to be used for large-scale production, a new design for the crucible and furnace would be necessary.

At the present time it has not been proven that the amount of oxygen in the final metal is directly related to the oxygen intensity ratio of the yttrium fluoride. If the amount of oxygen in the yttrium fluoride must be reduced to the lowest possible value, the preparation of the fluoride from the oxide using ammonium bifluoride shows little promise.

On the other hand, if an oxygen intensity ratio of approximately 0.40 to 0.50 is satisfactory, the process based on the conversion of the oxide to the fluoride using ammonium bifluoride should be given serious consideration in selecting a large scale process.